NATIONAL BUREAU OF STANDARDS REPORT

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Progress Report

on

Segregation in Dental Gold Casting Alloys

U.S. DEPARTMENT OF COMMERCE

NATIONAL BUREAU OF STANDARDS

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on

Segregation in Dental Gold Casting Alloys

By

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and

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Segregation in Dental Gold Casting Alloys

Abstract

The purpose of this investigation was to establish a quantitative method for determining the degree of segregation in dental gold casting alloys. The electron micro-probe was employed to analyze concentration differences between areas less than five microns apart. A line scan was used to determine the variations in concentration present in the alloy. The nature of the segregation was expressed by the coefficient of correlation, the frequency distribution, and the coefficient of variation. Segregation occurred between Ag and Cu in the Type I alloys. In the Type II and III alloys Ag and Pd segregated together and opposed Cu, while Ag, Cu, and Pt opposed Pd in the Type IV alloys. Au and Zn did not appear to segregate to a significant degree with the other elements in any of the alloys investigated. The coefficient of variation was used to define the degree of segregation on a quantitative basis. The degree of segregation between the fine grained alloys and coarse grained alloys of the same type was not significantly different. Pd was found to have the highest degree of segregation, while Au and Pt segregated the least. As the concentration of Cu was increased in the alloy, the degree of segregation decreased.

1. Introduction

Corrosion of dissimilar metals used in the same mouth to restore lost tooth structure has been a problem in dentistry for many years [20,25,26,27]. It has been shown [25,26] that galvanic currents are generated between dissimiliar metals causing tarnish and corrosion of restorations.

Corrosion of restorations made from gold casting alloys also occurs in some patients even though restorations made from other alloys are not present in the mouth. It has been shown [9,24,26] that intracrystalline segregation is often found in dental gold casting alloys in the form of dendritic structure which has been suggested [26,28] as a reason for this type of corrosion. Hedegard [9] has further demonstrated that corrosion can be greatly reduced when the restorations are given a homogenizing heat treatment.

Studies of the amount of segregation in gold alloys have usually depended upon microscopic examination of the polished and etched surface of the alloy [16,29]. It has been assumed that the absence of dendrites in a micrograph indicates that the alloy is homogeneous. The actual degree of segregation and small departures from homogeneity cannot, however, be determined by this method. Furthermore, the microstructure of a gold alloy is dependent upon its chemical composition and grain size [3,6,31].

It would appear from inspection of the polished and etched surface of a gold alloy, that reduction in grain size reduces the degree of segregation. Wagner [29] conducted an investigation to compare segregation in fine grained and coarse grained alloys in which the response of the polished surfaces to etching was used for evaluating homogeniety. Wagner [29,30] concluded that fine grained gold alloys were more homogeneous than coarse grained alloys.

The purpose of this investigation was to establish a method for determining the degree of segregation in dental gold casting alloys. The electron probe, a recently developed instrument which is capable of analyzing very small areas by means of x-ray emission methods, [2,3,4,5,10,11,14,17,21],

was used to investigate the degree os segregation. The degree of segregation was then correlated with the chemical composition of the alloys as determined from alloying formulas and by x-ray emission analysis, [8,15], and with the grain size of the alloy as determined by Jefferies' Planimetric Method[13].

2. Materials and Methods

2.1 Materials

The dentist may choose from four different types of dental gold casting alloys depending upon what type of restoration is to be constructed. The physical and chemical requirements for each type are listed in the American Dental Association Specification No. 5 for Dental Casting Gold Alloys [1].

One alloy typical of each of the four types of dental gold casting alloy was chosen for this investigation. Each alloy was obtained in both the coarse grained and fine grained state. The chemical composition of each alloy is listed in Table 1.

2.2 Methods of Testing

Chemical Composition -- The chemical composition of each alloy was determined from both alloying formulas and by x-ray emission methods [8,15]. The alloying formulas were those provided by the manufacturer.

One specimen of each alloy, both fine grained and coarse grained, was cast into a flat disk approximately 1.0 mm thick and having a diameter of 32 mm. The "lost-wax casting technic" [20,26] was utilized with a gypsum bound investment. An electric inductance furnace connected to a centrifugal casting machine, with a pyrometer attached to measure the temperature to within ± 15°C, was employed to melt and cast the alloys in molds preheated for two hours at 650°C. The specimens were quenched in a water bath immediately after casting, removed from the investment mold, and mounted in methyl methacrylate resin to facilitate surface preparation and x-ray analysis. Surface preparation was obtained by finishing with 600 wet silicon carbide grit. Each specimen was analyzed five times using an ARL-PXQ x-ray emission unit[1] and the x-ray intensity data were corrected by means of the Lucas-Tooth and Price Equation [15] as described by Eick et al [8].

Grain Size Determination -- In order to simulate the volume and surface area of a dental casting, conical specimens having a base of 6 mm and a side of 10 mm were cast using the "lost-wax casting technic" [20,26]. The wax patterns were prepared by pressing softened regular casting was into a split teflon mold. The patterns were cooled in water at room temperature, cut flush at the base, and an 8 gauge wax sprue was attached perpendicular to the center of the base. The wax patterns were then invested in a gypsum bound investment using the Whip-Mix Vac-U-Vestor.

Again an electric inductance furnace connected to a centrifugal casting machine was employed to heat the alloys to approximately 50°C above their liquidus temperature and to cast them immediately into molds preheated for one and one half hours at 650°C. The castings were allowed to cool in air for two minutes and were then quenched in water at room temperature. Six grams of alloy, about twice the weight of one cone, were used for casting each specimen.

The cones were mounted in methyl methacrylate resin and sectioned along the long axis with a water-cooled, fine toothed saw. One half of each cone was mounted again and surfaced through 600 silicon carbide grit.

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[1] Spectrochemical Analysis Section, National Bureau of Standards, Washington, D. C.

It was difficult to obtain a final polish on the Type I alloys (A and a) because cold worked metal tended to smear out on their surface. The method which gave the most satisfactory results was the use of a slurry of aluminum oxide (Al_2O_3) of 0.3 micron particle size in distilled water on a rotating velvet cloth. The remaining alloys (B,b,C,c,D, and d) were successfully polished with 1 micron diamond paste on a DP - cloth (MOL).

The specimens were then etched to delineate their dendritic structure and grain boundries. The technique chosen for Type I and II alloys (A,a,B, and b) was a two step procedure:

1. The specimens were electrolitically etched on a rotating cloth (13,23) using a 20 ma DC current and an electrolyte consisting of 4 g of potassium thiocyanate (KSCN), 4 g of ammonium chloride (NH_4Cl), and 4 g of ammonium thiosulfate [$(NH_4)_2\ S_2O_3$] in 200 ml of distilled water. Etching time was approximately 30 seconds.

2. The specimens were then etched with aqua regia, a mixture of 9 parts of hydrochloric acid (HCl) and 1 part of nitric acid (HNO_3). The specimens were immersed in the aqua regia for various lengths of time until the grain boundries were easily visible.

The Type III and IV alloys (C, c, D, and d) were etched in a mixture of equal amounts of 20% ammonium peroxydisulfate [$(NH_4)_2\ S_2O_8$] in distilled water and saturated potassium cyanide (KCN) in distilled water [31].

The grain size of each specimen was determined by using Jefferies' Planimetric Method [13].

The grain size was obtained in five positions on three samples of each alloy in both the fine grained and coarse grained state. The five positions were equally spaced from tip to base along the long axis of the specimen as shown in Figure 1.

Electron Probe Measurements -- After the grain size of the specimens had been determined, one sample of each alloy was resurfaced with 600 grit wet silicon carbide paper and polished with 1 micron diamond paste on a DP - cloth (MOL). A sample consisted of one specimen of fine grained alloy and one specimen of coarse grained alloy mounted next to one another. The tip and base of each specimen was indented with Knoop Indentations which were used as reference marks for the electron probe. This configuration is shown in Figure 2.

An ARL-EMX Electron Probe Micro-Analyzer[1] was used in this investigation. A line 480μ long was scanned by the electron beam (Figure 2) by automatically moving the sample at the rate of 96 μ/min, while the x-ray emission intensity of two elements was automatically recorded on charts moving at 3 cm/min. The sample was brought back to the starting position, the settings on one scanner were changed in order to detect another element, and the same line scanned again. This same procedure was repeated until x-ray emission data for all the elements in the specimen had been obtained. The graphs were calibrated before each run so that the background x-ray emission intensity read zero on the graph. The operating parameters for these determinations are listed in Table 2.

A micrograph of each section was taken showing the area over which the electron beam traveled. Each sample was then etched, as described previously, revealing the microstructure of each area. In this way, the microstructure of the alloy was correlated with specific points on the graphical plots of x-ray emission data for each element.

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[1] Spectrochemical Analysis Section, National Bureau of Standards, Washington, D. C.

3. Results

3.1 Chemical Composition

The alloying formulas as supplied by the manufacturer are listed in Table 1. The chemical compositions of the four alloys in both the fine grained and coarse grained state as determined by x-ray emission analysis [8] are listed in Table 3.

The chemical compositions of the alloys as determined by x-ray emission analysis agreed with those supplied by the manufacturer within the experimental error of this procedure. The fine grained and coarse grained alloys of any one type had basically the same chemical composition, as illustrated in Table 3.

3.2 Grain Size

A typical microstructure of a coarse grained and fine grained alloy of the same composition is given in Figure 3. The difference in grain size was well delineated. There also seemed to be a difference in the degree of segregation or, at least, in the type of segregation. The coarse grained alloy had grains of irregular shape and dendritic patterns were clearly visible. The fine grained alloy, however, had small relatively equiaxed grains and no dendritic structure could be seen.

The number of grains per mm^2 and the average diameter of the grains for the four types of alloys are presented in Table 4.

The diameter of the coarse grained alloy was approximately four times greater than the diameter of the fine grained alloy of Type I and in the order of ten times greater for the other three types.

Statistically significant differences between the grain sizes of alloys of different types were tested using a two-sided t-test [7,12,18] and a chosen confidence level of 95%. The results for the coarse grained alloys are listed in Table 5 and those for the fine grained alloys are presented in Table 6.

A two sided t-test at the 95% confidence level was also employed to study the grain size distribution within each specimen. The two counted positions closest to the tip in each specimen were taken as areas characteristic of the tip of the cone (Figure 1) while the base was represented by the two positions closest to the base. The results of these comparisons are shown in Table 7.

The value obtained for the grain size at the base was larger than that at the tip in all cases. However, this difference was significant in only four of the cases.

3.3 Electron Probe Data

Electron Probe Results - The tip and the base of each specimen were analyzed by the electron probe beam along a line 480μ long. The variation in composition for each element was reocrded graphically with a distance of 1 cm on the graph representing a distance of 32μ on the specimen. Two micrographs of each section were taken showing the area over which the electron beam traveled and the microstructure of the probed area. In this way, the microstructure of the alloy was correlated with specific points on the graphical plots.

The height of the curve was recorded for each element at a distance of 1/2 centimeter on the graph so that a total of 30 points were obtained. Since the electron probe had been adjusted so that zero concentration of an element was represented by the base line on a graph, the

average height of the 30 points represented the mean composition by weight as determined previously from alloying formulas and x-ray emission methods. In this manner, the height of each of the 30 points was correlated with a specific percent concentration value. For example, the micrographs showing the area over which the electron beam traveled and the microstructure of the probed area are shown in Figures 4 and 5 respectively for the base of the Type III coarse grained alloy. The graph of the variation in composition for each element is shown in Figure 6. Table 8 contains the percent concentration by weight at each of the 30 points for all the elements present in this alloy.

When specific points of the microstructure shown in Figure 5 were correlated with the electron probe graph shown in Figure 6, it could be concluded that the dendrites had high concentrations of Pd and Ag while the matrix was rich in Cu. From the electron probe graph it is apparent that Au did not segregate appreciably, while Pd, Cu, Zn, and Ag appeared to segregate to a greater extent.

The two micrographs, the electron probe graph, and the percent concentration by weight of each element for the tip of the Type III, fine grained alloy are shown in Figures 7, 8, and 9 and in Table 9 respectively. When specific points of the microstructure shown in Figure 8 were correlated with the electron probe graph shown in Figure 9, it could be concluded that the center of the grains had a high concentration of Pd and Ag and the Cu was concentrated near the grain boundries.

The reproducibility of the electron probe graphs was determined by scanning the same line several times while recording the x-ray emission data of a particular element. For example, the reproducibility for the concentration of Pd in the tip of the Type III, fine grained alloy is shown in Figure 10 for two line scans. The reproducibility error was determined by calculating the average difference in concentration for the 30 points along the line scan. Pd exhibited the maximum error which was 1.0% of the concentration present. The average error for all the elements was 0.5% of the concentration present. Thus the error in reproducing the variation in concentration for each element was very small.

Correlation Coefficient -- The coefficient of correlation [7,12] is a statistic that can be employed to determine whether the concentration values of one element parallel or oppose that of another element. The values of the coefficient of correlation are between a -1.0 and a +1.0 depending upon whether the concentration values of two elements have a negative or positive correlation. For example, a -1 coefficient of correlation indicates that if one element is at a point of high concentration, the other element is at a point of low concentration.

The coefficients of correlation were calculated from the 30 concentration points of each element obtained from the line scans. The coefficients of correlation for all element combinations at the four positions investigated on the Type I alloys, together with their confidence range at the 95% confidence level, are listed in Table 10. A statistically significant negative correlation was found between Ag and Cu. This indicates that when the concentration of Ag was high the concentration of Cu was low. There was no strong correlation between Au and Ag or between Au and Cu.

The coefficients of correlation and the confidence range at the 95% confidence level for all element combinations of the four positions on the Type II, III, and IV alloys are listed in Tables 11, 12, and 13 respectively. A strong negative correlation was found between Ag and Cu for the Type II and III alloys, but a statistically significant positive correlation was found in the Type IV alloys. Ag and Pd had a positive correlation in Type II and a stronger positive correlation in Type III. In Type IV, however, there was a significant negative correlation between Ag and Pd. There

was a negative correlation between Cu and Pd for Types II, III, and IV. In the Types II, III, and IV alloys the Zn did not appear to segregate in any definite pattern, since there was no strong negative or positive correlation with the other elements. In the Type IV alloy there was a significant positive correlation between Au and Pt.

The averages of the coefficients of correlation for Ag-Cu, Ag-Pd, Cu-Pd, Cu-Zn, and Pd-Zn for the four types of alloys are listed in Table 14.

In summary, in the Type I alloys, Ag opposed Cu, in the Types II and III alloys Ag and Pd opposed Cu, and in the Type IV alloys Pd opposed Ag, Cu, and Pt.

Frequency Distribution -- One way to represent the degree of segregation was by means of a histogram [7,12]. The thirty concentration values taken from the line scans were placed in intervals and plotted in the form of a histogram. For example, intervals of 2.0% for Au, 0.3% for Ag, 0.2% for Cu, 0.2% for Pd, and 0.1% for Zn were chosen and the data obtained from the base of the Type II, fine grained alloy were plotted in this manner. Figures 11, 12, 13, 14, and 15 are the histograms obtained for Au, Ag, Cu, Pd, and Zn respectively. The data for Au, Ag, and Zn produced a fairly normal distribution for this alloy. The data for Cu produced a distribution that appeared to be skew to the right, while that for Pd was skew toward the left.

Coefficient of Variation -- The variation in composition about the mean can be expressed by the variance or standard deviation. In order to express the standard deviation on a percent basis, it can be divided by the mean to give the coefficient of variation. Thus, the degree of variation or the degree of segregation can be expressed by the coefficient of variation [7].

The standard deviation for each set of thirty points was calculated and then divided by the mean concentration to obtain the coefficient of variation. The degree of segregation for Au, Ag, and Cu as expressed by the coefficient of variation for the four positions investigated on the Type I alloys is listed in Table 15. The degree of segregation for the Type II, III, and IV alloys is listed in Tables 16, 17, and 18 respectively.

According to Raybold, Cameron, and Youden [22] the distribution of the coefficient of variation is very similar to that of the standard deviation. Thus, the F distribution may be used to test whether there is a statistically significant difference between two coefficients of variation. If the ratio of the squared coefficients of variation is greater than a specific value given in the F table, there is a significant difference between the two coefficients of variation.

The difference in segregation between the tip and base was tested by averaging the two coefficients of variation squared for the tip, averaging the two coefficients of variation squared for the base, and comparing their ratio with the value obtained from the F table. In this case, there were 30 points for each position, so the F value with 58 degrees of freedom (30+30-2) at the 99% confidence level was 2.03. This procedure was performed for each element and for each type, so that a total of 19 comparisons were made. For example, from Table 15, the values for gold at the tip of the fine grained and coarse grained positions were squared and averaged

$$\left(\frac{(1.53)^2+(2.35)^2}{2} = \frac{7.863}{2} = 3.932\right)$$

the values for gold at the base of the fine grained and coarse grained positions were squared and averaged

$$\left(\frac{(4.44)^2+(1.60)^2}{2} = \frac{22.274}{2} = 11.137\right),$$

and the ratio of these values compared ($\frac{11.137}{3.932} = 2.83$). In this case, there was a significant difference between the degree of segregation in the tip and base with the base having a higher degree of segregation. From the 19 comparisons made, 4 were significant (Au-Type I, Cu-Type I, Zn-Type III, and Au-Type IV) with the base having a higher degree of segregation than the tip and one was significant (Ag-Type IV) with the degree of segregation being higher in the tip.

A similar procedure was employed to test if there was a significant difference between the fine grained and coarse grained alloys of the same type. In four of the nineteen comparisons (Au-Type I, Cu-Type II, Zn-Type II, and Zn-Type III) the degree of segregation was greater in the fine grained alloy as compared with the coarse grained alloy. In two positions (Au-Type II and Ag-Type IV) the degree of segregation was greater for the coarse grained alloy. alloy.

The average degree of segregation of each element for each type of alloy is listed in Table 19.

A comparison between the degree of segregation of each element in a particular type alloy was performed. Tables 20, 21, 22, and 23 give the results of these comparisons for Types I, II, III, and IV respectively. For example, from Tables 19 and 21 it can be concluded that Pd has the highest degree of segregation for the Type II alloys followed by Zn, Cu, Ag, Au and there was a significant difference between the degree of segregation of each element.

A comparison between the degree of segregation of a particular element within the four types of alloys was also performed. The results for Au, Ag, Cu, Pd, and Zn are reported in Tables 24, 25, 26, 27, and 28 respectively. For example, from Tables 19 and 26, the degree of segregation for Cu was the greatest in Type I and decreased a significant amount for Types II, III, and IV.

4. Discussion

The electron micro-probe was an excellent instrument for quantitatively measuring the degree of segregation in gold alloys. The electron beam could be focused so that the differences in concentration of an element could be observed on the intragranular scale. Very small differences in concentration could be distinguished and the difference in concentration of areas that were less than five microns apart could be determined By performing a line scan with the electron probe a sufficiently large area that was characteristic of the amount of segregation in the alloy could be investigated. Since the electron probe could be adjusted so that the x-ray background intensity represented zero on the recording graph, every point on the line scan could be assigned a specific concentration value.

The electron micro-probe provided numerical data that were used to define the degree of segregation. The results from these measurements became much more meaningful when statistical methods were employed. The three statistical methods employed in this investigation were the coefficient of correlation, the frequency distribution, and the coefficient of variation.

The coefficient of correlation aided greatly in establishing which elements segregated together or opposed one another. The statistical limits on the coefficient of correlation were rather large when the actual value was near zero. In fact, a value of +0.4 or -0.4 for the correlation coefficient was necessary before a meaningful positive or negative correlation could be established. When the coefficient of correlation was close to +1.0 or -1.0, the range became much smaller and a much more significant correlation was established.

The coefficients of correlation for Au and those for Zn indicated that these two elements did not strongly segregate with any of the other elements.

It was rather surprising that most of the Zn did not solidify in the interdentritic regions or at the grain boundries, since the melting point of Zn was relatively low. It would be expected that Zn should solidify in the regions that solidified last.

In the Type I alloys there was a strong negative coefficient of correlation between Ag and Cu. Thus, in this type of alloy the segregation occurred between Ag and Cu. This situation would be expected, since the binary phase diagram for Ag and Cu indicated that these two elements form a eutectic alloy.

In the Type II and III alloys Ag and Pd opposed Cu. Again, this could be explained from the fact that Ag and Cu form a eutectic alloy, while Ag and Pd form a solid solution. Thus, Ag and Pd would readily intermix, while Cu would not be miscible to any large degree.

In the Type IV alloys, Ag, Cu, and Pt opposed Pd. This type of alloy was the only one that contained Pt. Apparently the Pt eliminated the effectiveness of the Ag - Cu eutectic and caused the Ag to solidify with Cu. The binary phase diagram for Ag and Pt indicates that a series of intermetallic compounds are formed. Also the atomic diameter of Ag (2.882 A°) is closer to that of Pt (2.769 A°) than to that of Pd (2.745 A°). The lowest energy state for Ag would be in combination with Pt and not with Pd. Apparently, the lowest energy state for Cu was also obtained by combining with Pt instead of Pd. Thus, Ag, Cu, and Pt combined together and opposed Pd.

The frequency distribution plotted in the form of a histogram indicated the type of distribution for a particular element. Au, Ag, and Zn generally produced a normal distribution, while Cu produced a distribution that appeared to be skew to the right and that for Pd was skew toward the left. A skew distribution to the right such as that exhibited by Cu would indicate that areas were more likely to have a high concentration of the element than a low concentration. On the other hand, a skew distribution to the left similar to that of Pd would indicate that areas were more likely to be deficient of the element. The width of the distribution also indicated the relative degree of segregation. This technic for expressing the degree of segregation did not, however, give numerical quantity, so that comparisons between the degree of segregation of different elements and positions could not be made.

The coefficient of variation provided a quantitative measure for the degree of segregation in these alloys and allowed comparisons of the degree of segregation to be made. Since the coefficient of variation is a normalized quantity and expresses the amount of variation in concentration independent of the mean concentration, a comparison of the amount of segregation between different elements that were present in varying concentrations could be performed. Significance levels could be established since the distribution of the coefficient of variation was very similar to that of the variance. Therefore, the F distribution could be employed.

By comparing the degree of segregation as expressed by the coefficient of variation, it was established that there was not a significant difference between the amount of segregation in the tip and in the base of the cone. This comparison further established that there was no significant difference between the degree of segregation of the fine grained alloys and that of the coarse grained alloys of the same type. The alloying formulas and chemical analysis by x-ray emission techniques established that there was no difference in the chemical composition between the fine grained and coarse grained alloys of the same type. The reduction in grain size apparently occurred as a result of the addition of about 50 parts per million of Irridium or Ruthenium as described by Nielsen and Tuccillo [19].

The statement made by Wagner [29] that fine grained alloys are more homogeneous than coarse grained alloys, therefore, is not consistent with the data obtained in this study. The results of this investigation strongly

indicated that there was no significant difference between the degree of segregation of the fine grained alloy and coarse grained alloy of the same type. This investigation further established that the condition of the etched surface of an alloy was not always a true indication of the amount of segregation present in the alloy.

By expressing the degree of segregation in terms of the coefficient of variation, it was established that Pd exhibited the highest degree of segregation. Cu and Zn had the next highest degrees of segregation. Au, Pt and Ag, on the other hand, did not segregate to a large extent. It was further established that as the chemical concentration of Cu increased, its degree of segregation decreased.

The electron micro-probe proved to be an excellent instrument for measuring the degree of segregation. A quantitative technique for measuring the degree of segregation was established, so that the reliance by the metallurgist solely on micrographs to observe the amount of segregation in an alloy is no longer necessary.

5. Summary

The purpose of this investigation was to establish a quantitative method for determining the degree of segregation in dental gold casting alloys. The electron micro-probe was employed to analyze small concentration differences between areas that were less than five microns apart. A line scan was used to establish the variations in concentration over a large enough area to be typical of the amount of segregation present in the alloy. The nature of the segregation was expressed by the coefficient of correlation, the frequency distribution, and the coefficient of variation. The degree of segregation was correlated with the chemical composition of the alloy as determined from alloying formulas and x-ray emission methods, and with the grain size of the alloy as determined by Jefferies' Planimetric Methods.

The coefficient of correlation established that segregation occurred between Ag and Cu in the Type I alloys. In the Type II and III alloys Ag and Pd segregated together and opposed Cu, while Ag, Cu, and Pt opposed Pd in the Type IV alloys. Au and Zn did not appear to segregate to a significant degree with the other elements in any of the alloys investigated.

The coefficient of variation was used to define the degree of segregation on a quantitative basis. It was found that the degree of segregation between the fine grained alloys and coarse grained alloys of the same type was not significantly different. Pd was found to have the highest degree of segregation, while Au and Pt segregated the least. As the concentration of Cu was increased in the alloy, the degree of segregation decreased.

It was further established that the degree of segregation in an alloy was measured much more accurately by means of the electron probe than by examination of the etched surface of the alloy.

6. Conclusions

1. The use of the electron micro-probe provided an excellent method of quantitatively measuring the degree of segregation in an alloy.

2. The coefficient of correlation established whether one element segregated with another element or opposed another element.

3. In the Type I alloys Ag opposed Cu; in the Type II and III alloys Ag and Pd opposed Cu; in the Type IV alloys Ag, Cu, and Pt opposed Pd.

4. The coefficients of variation provided a quantitative method of defining the degree of segregation that could be compared with one another.

5. There was no significant difference between the degree of segregation of a coarse grained alloy and a fine grained alloy of the same type.

6. There was no significant difference between the degree of segregation of the tip and base of a specimen of the same type of alloy.

7. Pd had the highest degree of segregation.

8. Au and Pt had the lowest degree of segregation.

9. The degree of segregation of Cu decreased as the concentration of Cu increased.

10. The amount of segregation in an alloy was more precisely measured by the electron micro-probe than by observation of the polished and etched surface of the alloy.

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Table 1

Chemical Composition of Gold Alloys

Type		I	II	III	IV
Code	Coarse Grained	A	B	C	D
	Fine Grained	a	b	c	d
Percent Composition*	Au	91.65	77.6	74.0	68.5
	Ag	4.65	12.6	11.5	12.0
	Cu	3.70	7.2	9.5	11.0
	Pt	0.00	0.0	0.0	2.5
	Pd	0.00	2.0	4.0	4.0
	Zn	0.00	0.7	1.0	2.0
	Total	100.00	100.1	100.0	100.0

* Alloying formulas as supplied by the J. M. Ney Co., Hartford, Connecticut.

Table 2

Operating Parameters for Electron Micro-Probe

Element	Scanner	Crystal	Wave Length
Au	I	LiF	1.277
Ag	II	EDT	4.754
Cu	I	LiF	1.542
Pd	II	EDT	4.368
Pt	I	LiF	1.313
Zn	I	LiF	1.437

Kev = 20 Specimen Current = 0.42 μ Amps

Table 3

Chemical Composition as Determined by X-Ray Emission Analysis

Alloy+	Au*	Ag*	Cu*	Pd*	Pt*	Zn*	Total
A	91.7	4.3	3.8	0.0	0.1	0.0	99.9
a	91.6	4.4	3.7	0.0	0.1	0.0	99.8
B	77.9	12.2	7.3	1.9	0.0	0.6	99.9
b	77.8	12.3	7.3	1.9	0.0	0.6	99.9
C	74.3	11.2	9.3	3.8	0.0	0.9	99.5
c	74.1	11.1	9.7	3.8	0.0	1.0	99.7
D	68.8	11.8	11.2	4.0	2.5	2.0	100.3
d	68.7	11.8	11.3	4.0	2.4	2.1	100.3

* Percent concentration by weight reported to the nearest 0.1%.

+ Code as described in Table 1.

Table 4

Grain Size of Coarse and Fine Grained Alloys

Alloy	Grains per mm^2	Coefficient of variation, %	Average diameter of grain, microns
A	28.00*	21.7	213
B	5.10	22.5	500
C	4.88	30.3	511
D	8.08	38.3	397
a	480	28.5	52
b	652	24.0	44
c	638	31.7	45
d	640	35.4	45

* Each value is an average of 15 counted areas.

Table 5

Differences of Grain Size Between
Coarse Grained Alloys

Coarse grained alloys	B	C	D
A	+	+	+
D	+	+	
C	-		

+ There is a significant difference

- There is no significant difference

Table 6

Differences of Grain Size Between
Fine Grained Alloys

Fine grained alloys	b	c	d
a	+	+	+
d	-	-	
c	-		

+ There is a significant difference

- There is no significant difference

Table 7

Difference of Grain Size Between
Tip and Base of Cone

Alloy	Grains per mm^2		Significance of difference
	Tip	Base	
A	20.77	20.26	-
B	5.94	4.69	-
C	5.79	4.13	+
D	8.79	7.75	-
a	583	392	+
b	781	613	-
c	767	504	+
d	808	458	+

+ There is a significant difference

- There is no significant difference

Table 8

Type III

Coarse Grained, Base

Point	Au*	Ag*	Cu*	Pd*	Zn*
1	74.1	11.9	8.8	4.9	1.0
2	74.1	11.6	9.2	4.7	0.9
3	74.1	11.9	9.0	5.0	1.0
4	74.1	11.9	8.8	5.0	0.9
5	74.1	11.9	8.8	5.2	1.0
6	75.6	11.4	9.4	3.8	0.9
7	72.6	11.6	9.2	4.7	1.0
8	74.1	11.4	9.4	3.8	1.0
9	75.6	11.4	9.6	3.5	0.9
10	74.1	11.6	9.4	4.3	1.0
11	74.1	11.6	9.4	4.4	1.0
12	75.6	11.0	10.0	2.6	0.9
13	75.6	11.4	9.6	3.1	1.0
14	74.1	11.2	9.8	3.5	1.0
15	74.1	11.2	9.6	3.6	1.0
16	74.1	11.2	9.8	3.7	1.0
17	75.6	11.2	10.0	3.0	1.0
18	74.1	11.2	9.8	3.4	1.0
19	72.6	11.6	9.4	4.4	1.0
20	74.1	11.4	9.4	4.2	1.0
21	74.1	11.6	9.6	4.0	1.0
22	74.1	11.6	9.2	4.3	1.0
23	72.6	11.6	9.6	4.0	1.1
24	74.1	11.2	10.0	3.4	1.0
25	74.1	11.2	10.0	3.0	1.0
26	72.6	11.6	9.2	4.4	1.0
27	72.6	11.2	10.0	3.6	1.1
28	74.1	11.0	10.4	2.6	1.1
29	72.6	11.9	8.8	4.9	0.9
30	72.6	11.6	9.4	4.4	1.0

* Percent concentration by weight reported to the nearest 0.1%.

Table 9

Type III

Fine Grained, Tip

Point	Au*	Ag*	Cu*	Pd*	Zn*
1	76.0	11.8	9.2	4.5	1.1
2	73.3	12.0	8.6	5.4	1.1
3	74.6	11.1	9.6	3.9	1.0
4	74.6	11.3	9.6	3.3	0.9
5	74.6	11.8	8.8	4.3	0.9
6	73.3	11.8	9.0	5.0	1.0
7	76.0	11.3	9.4	4.0	1.0
8	76.0	11.1	10.2	2.9	0.9
9	74.6	11.3	9.6	3.7	1.0
10	76.0	11.5	9.6	3.8	0.9
11	74.6	11.5	9.6	4.0	1.0
12	76.0	11.8	9.4	4.4	1.1
13	74.6	11.3	9.8	3.4	1.2
14	74.6	11.8	9.0	4.6	1.1
15	74.6	11.8	9.4	4.2	1.0
16	74.6	11.1	10.2	2.9	1.0
17	74.6	11.3	9.8	3.8	1.0
18	73.3	11.5	9.2	4.6	1.0
19	73.3	11.5	9.6	3.9	1.0
20	73.3	11.3	9.6	3.7	1.0
21	73.3	11.8	9.0	5.0	1.0
22	73.3	11.1	9.6	3.4	0.9
23	73.3	11.5	9.6	4.3	1.0
24	73.3	11.1	10.0	3.2	1.1
25	73.3	10.9	10.4	2.4	1.0
26	72.0	12.0	8.8	5.0	1.0
27	72.0	12.0	8.8	5.2	1.0
28	72.0	11.5	9.4	4.6	1.0
29	72.0	11.1	10.0	2.7	0.9
30	72.0	11.5	9.4	4.0	1.0

* Percent concentration by weight reported to the nearest 0.1%.

Table 10

Correlation Coefficients for Type I Alloys

Alloy		Au - Ag	Au - Cu	Ag - Cu
Fine Grained Tip	C.C.*	.24	.08	-.80
	C.L.+	-.13 .55	-.28 .42	-.89 -.59
Fine Grained Base	C.C.	.51	.21	-.66
	C.L.	.17 .73	-.17 .52	-.82 -.37
Coarse Grained Tip	C.C.	.52	.06	-.68
	C.L.	.17 .73	-.31 .41	-.83 -.42
Coarse Grained Base	C.C.	.43	.12	-.60
	C.L.	.06 .67	-.27 .46	-.78 -.27

* Coefficient of correlation.

\+ Confidence range for the correlation coefficient at the 95% confidence level.

Table 11

Correlation Coefficients for Type II Alloys

Alloy		Au - Ag	Au - Cu	Au - Pd	Au - Zn
Fine Grained Tip	C.C.*	-.21	.24	-.47	.27
	C.L.+	-.53 .18	-.13 .56	-.71 -.12	-.13 .58
Fine Grained Base	C.C.	.18	.02	-.10	.31
	C.L.	-.21 .48	-.36 .37	-.44 .28	-.08 .62
Coarse Grained Tip	C.C.	.11	.34	-.15	.34
	C.L.	-.28 .45	-.04 .64	-.48 .23	-.04 .64
Coarse Grained Base	C.C.	-.20	.15	-.13	.55
	C.L.	-.53 .18	-.23 .48	-.47 .24	.20 .76

* Coefficient of correlation.

\+ Confidence range for the correlation coefficient at the 95% confidence level.

Table 11

Correlation Coefficients for Type II Alloys (Continued)

Alloy		Ag - Cu	Ag - Pd	Ag - Zn	Cu - Pd	Cu - Zn	Pd - Zn
Fine Grained Tip	C.C.*	-.95	.29	-.47	-.28	.58	-.42
	C.L.+	-.98 -.89	-.10 .60	-.76 -.10	-.59 .12	.25 .78	-.67 -.03
Fine Grained Base	C.C.	-.90	.44	-.06	-.43	.30	-.55
	C.L.	-.96 -.78	.07 .68	-.43 .27	-.67 -.06	-.09 .58	-.76 -.20
Coarse Grained Tip	C.C.	-.71	.34	.20	-.55	.21	-.08
	C.L.	-.85 -.45	-.04 .64	-.20 .53	-.76 -.20	-.18 .53	-.44 .30
Coarse Grained Base	C.C.	-.84	.49	-.29	-.53	.29	-.32
	C.L.	-.93 -.68	.13 .73	-.60 .10	-.75 .17	-.10 .60	-.62 .08

* Coefficient of correlation.

\+ Confidence range for the correlation coefficient at the 95% confidence level

Table 12

Correlation Coefficients for Type III Alloys

Alloy		Au - Ag	Au - Cu	Au - Pd	Au - Zn	Ag - Cu	Ag - Pd	Ag - Zn	Cu - Pd	Cu - Zn	Pd - Zn
Fine Grained Tip	C.C.*	-.11	.20	-.19	.07	-.90	.91	.26	-.93	-.16	.28
	C.L.+	-.48 .25	-.18 .53	-.50 .20	-.30 .40	-.96 -.78	.76 .96	-.15 .56	-.97 -.84	-.49 .21	-.11 .58
Fine Grained Base	C.C.	-.02	.07	-.03	-.32	-.86	.91	-.45	-.94	.26	-.36
	C.L.	-.38 .37	-.30 .40	-.38 .37	-.62 .08	-.93 -.69	.76 .96	-.69 -.09	-.98 -.87	-.15 .56	-.64 .03
Coarse Grained Tip	C.C.	-.36	.54	-.68	-.02	-.88	.82	-.03	-.90	.17	.05
	C.L.	-.64 .03	.18 .75	-.83 -.42	-.38 .37	-.95 -.76	.61 .90	-.38 .36	-.96 -.78	-.22 .47	-.33 .42
Coarse Grained Base	C.C.	-.35	.26	-.48	-.41	-.93	.93	-.23	-.93	.40	-.20
	C.L.	-.63 .04	-.15 .56	-.72 -.11	-.65 -.02	-.97 -.84	.84 .97	-.54 .15	-.97 .84	.02 .67	-.53 .18

* Coefficient of correlation.

\+ Confidence range for the correlation coefficient at the 95% confidence level.

Table 13

Correlation Coefficients for Type IV Alloys

Alloy		Au - Ag		Au - Cu		Au - Pd		Au - Pt		Au - Zn		Ag - Cu		Ag - Pd		Ag - Pt		Ag - Zn		Cu - Pd	
	C.C.*	.67		.72		-.86		.66		-.57		.69		-.89		.76		-.55		-.87	
Fine Grained Tip	C.L.+	.38	.82	.46	.85	-.93	-.69	.37	.82	-.77	-.23	.44	.85	-.95	-.77	.53	.88	-.76	-.20	-.94	-.72
	C.C.	.36		.40		-.62		.84		-.51		.73		-.82		-.32		-.16		-.84	
Fine Grained Base	C.L.	-.03	.64	.02	.67	-.78	-.30	.68	.93	-.73	-.17	.48	.86	-.90	-.61	-.08	.62	-.49	.21	-.93	-.68
	C.C.	.73		.67		-.34		.58		-.16		.63		.25		.56		.31		-.24	
Coarse Grained Tip	C.L.	.48	.86	.38	.82	-.64	.04	.25	.78	-.49	.21	.32	.79	-.12	.57	.21	.77	-.10	.60	-.56	.13
	C.C.	.68		.75		-.82		.78		-.55		.69		-.78		.76		-.38		-.82	
Coarse Grained Base	C.L.	.42	.83	.51	.87	-.90	-.61	.57	.88	-.76	-.20	.44	.85	-.88	-.57	.53	.88	-.66	.01	-.90	-.61

Alloy		Cu - Pt		Cu - Zn		Pd - Pt		Pd - Zn		Pt - Zn	
	C.C.*	.73		-.20		-.80		.54		-.48	
Fine Grained Tip	C.L.+	.48	.86	-.53	.18	-.90	-.59	.17	.75	-.72	-.11
	C.C.	.40		.08		-.54		.36		-.31	
Fine Grained Base	C.L.	.02	.67	-.30	.44	-.75	-.17	-.03	.64	-.60	.10
	C.C.	.43		.20		-.04		.74		.12	
Coarse Grained Tip	C.L.	.06	.67	-.18	.53	-.42	.35	.49	.86	-.26	.46
	C.C.	.70		-.30		-.84		.69		-.66	
Coarse Grained Base	C.L.	.45	.87	-.58	.12	-.93	-.68	.44	.85	-.82	-.37

* Coefficient of correlation.

\+ Confidence range for the correlation coefficient at the 95% confidence level.

Table 14

Average Correlation Coefficients

Type		Ag - Cu		Ag - Pd		Cu - Pd		Cu - Zn		Pd - Zn	
I	C.C.*	-.68[x]									
	C.L.+	-.82	-.37								
II	C.C.	-.85		.39		-.45		.34		-.34	
	C.L.	-.93	-.69	.01	.64	-.71	-.07	-.04	.64	-.64	.04
III	C.C.	-.89		.89		-.92		.17		-.06	
	C.L.	-.96	-.76	.76	.96	-.96	-.82	-.22	.47	-.41	.31
IV	C.C.	.68		-.56		-.69		-.06		.58	
	C.L.	.37	.82	-.77	-.21	-.85	-.44	-.41	.31	.25	.78

* Coefficient of correlation.
\+ Confidence range for the correlation coefficient at the 95% confidence level.
[x] Average of four determinations (tip and base in both fine grained and coarse grained alloys).

Table 15

Degree of Segregation for Type I Alloys*

Alloy	Au	Ag	Cu
Fine Grained Tip	1.53	2.83	8.52
Fine Grained Base	4.44	5.05	16.14
Coarse Grained Tip	2.35	4.86	12.46
Coarse Grained Base	1.60	5.61	16.52

* Coefficient of variation, $\frac{S}{\bar{X}}$

Table 16

Degree of Segregation for Type II Alloys*

Alloy	Au	Ag	Cu	Pd	Zn
Fine Grained Tip	1.97	5.99	12.31	34.10	17.33
Fine Grained Base	0.95	4.37	7.99	28.68	13.53
Coarse Grained Tip	2.40	3.97	6.26	21.81	10.98
Coarse Grained Base	2.71	3.60	7.54	39.78	6.77

* Coefficient of Variation, $\frac{S}{\bar{X}}$

Table 17

Degree of Segregation for Type III Alloys*

Alloy	Au	Ag	Cu	Pd	Zn
Fine Grained Tip	1.75	2.77	4.72	19.07	7.16
Fine Grained Base	1.19	3.08	4.86	23.28	16.10
Coarse Grained Tip	1.51	2.36	5.22	18.91	7.67
Coarse Grained Base	1.30	2.37	4.38	18.27	5.53

* Coefficient of variation, $\frac{S}{\bar{X}}$

Table 18

Degree of Segregation for Type IV Alloys*

Alloy	Au	Ag	Cu	Pd	Pt	Zn
Fine Grained Tip	1.92	1.74	2.89	28.89	3.64	9.16
Fine Grained Base	3.12	1.71	2.77	29.21	2.42	8.20
Coarse Grained Tip	1.62	3.90	2.35	19.49	1.48	7.35
Coarse Grained Base	3.00	2.10	2.77	27.51	2.97	8.06

* Coefficient of variation, $\frac{S}{\bar{X}}$

Table 19

Average Degree of Segregation*

Type	Au	Ag	Cu	Pd	Pt	Zn
I	2.48	4.58	13.41	-	-	-
II	2.01	4.48	8.52	31.09	-	12.15
III	1.44	2.64	4.80	19.88	-	9.12
IV	2.42	2.36	2.70	26.27	2.63	8.19

* Coefficient of variation, $\frac{S}{\bar{X}}$

Table 20

Difference between the Degree of Segregation for Type I Alloys*

Element	Cu	Ag
Au	+	+
Ag	+	

* F ratio at the 99% confidence level.
+ There is a significant difference.

Table 21

Difference between the Degree of Segregation for Type II Alloys*

Element	Zn	Pd	Cu	Ag
Au	+	+	+	+
Ag	+	+	+	
Cu	+	+		
Pd	+			

* F ratio at the 99% confidence level.
+ There is a significant difference.

Table 22

Difference between the Degree of Segregation for Type III Alloys*

Element	Zn	Pd	Cu	Ag
Au	+	+	+	+
Ag	+	+	+	
Cu	+	+		
Pd	+			

* F ratio at the 99% confidence level.
+ There is a significant difference.

Table 23

Difference between the Degree of Segregation for Type IV Alloys*

Element	Zn	Pt	Pd	Cu	Ag
Au	+	-	+	-	-
Ag	+	-	+	-	
Cu	+	-	+		
Pd	+	+			
Pt	+				

* F ratio at the 99% confidence level.
+ There is a significant difference.
- There is no significant difference.

Table 24

Difference between the Degree of Segregation for Au*

Type	IV	III	II
I	-	+	-
II	-	+	
III	+		

Table 25

Difference between the Degree of Segregation for Ag*

Type	IV	III	II
I	+	+	-
II	+	+	
III	-		

Table 26

Difference between the Degree of Segregation for Cu*

Type	IV	III	II
I	+	+	+
II	+	+	
III	+		

Table 27

Difference between the Degree of Segregation for Pd*

Type	IV	III
II	-	+
III	+	

Table 28

Difference between the Degree of Segregation for Zn*

Type	IV	III
II	+	+
III	-	

* F ratio at the 99% confidence level.
+ There is a significant difference.
- There is no significant difference.

GRAIN SIZE DETERMINATION SPECIMEN

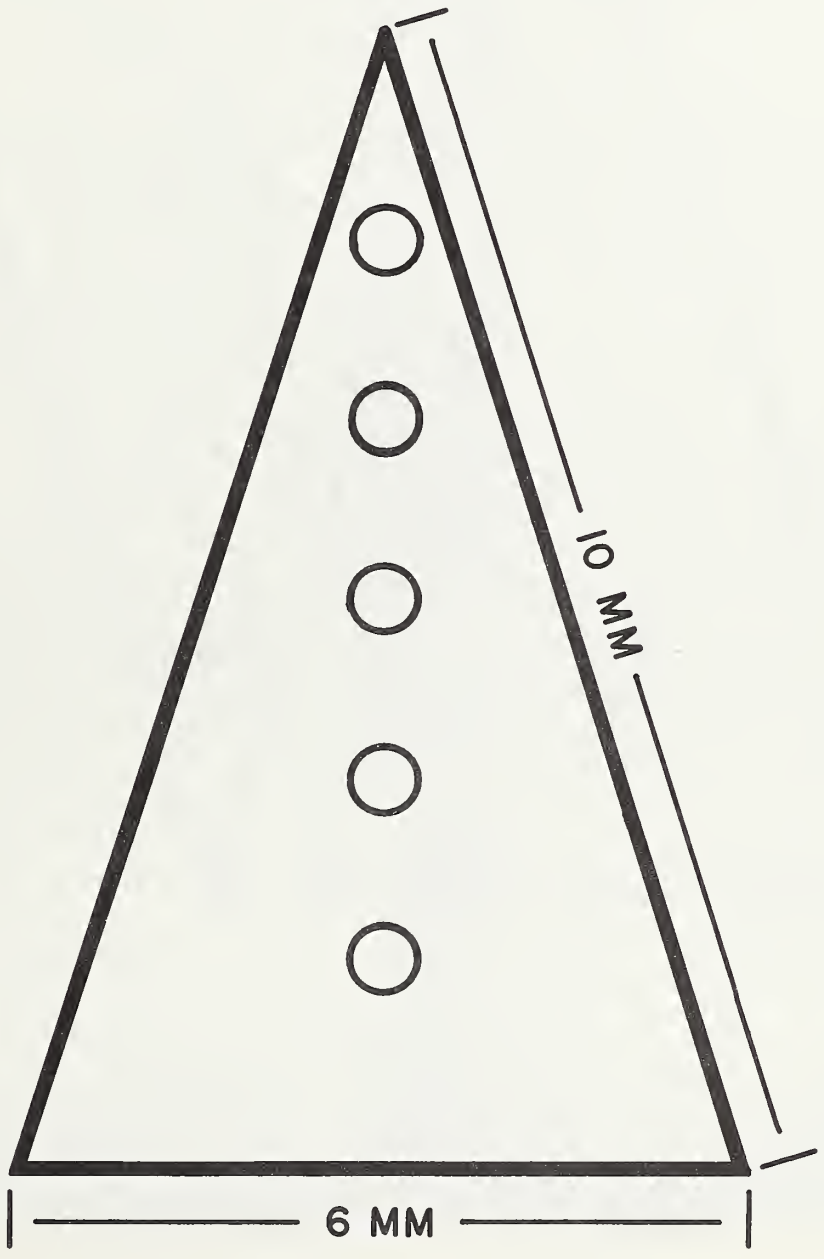

Figure 1. Grain size determination specimen.

ELECTRON PROBE SPECIMENS

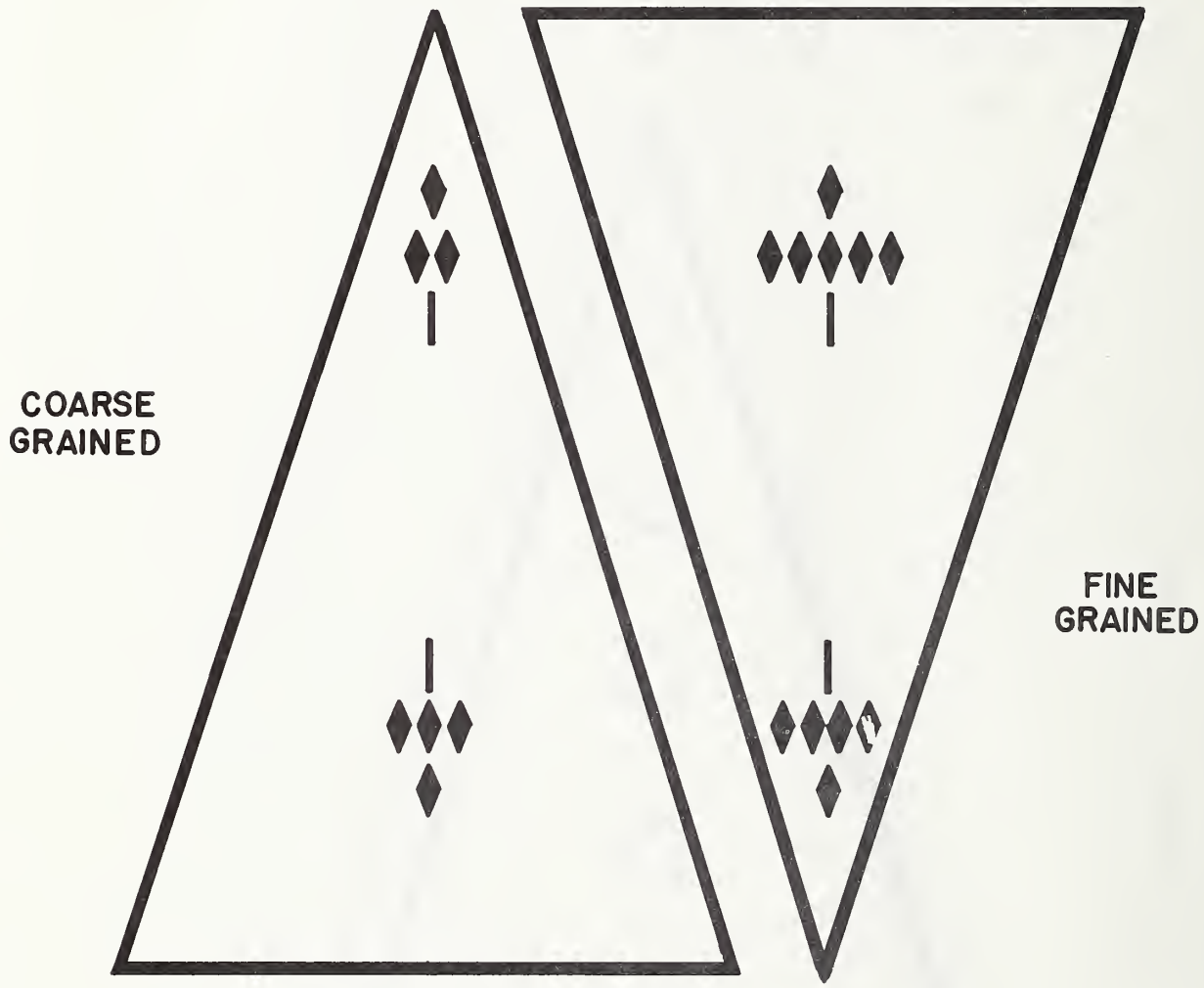

Figure 2. Electron probe specimens.

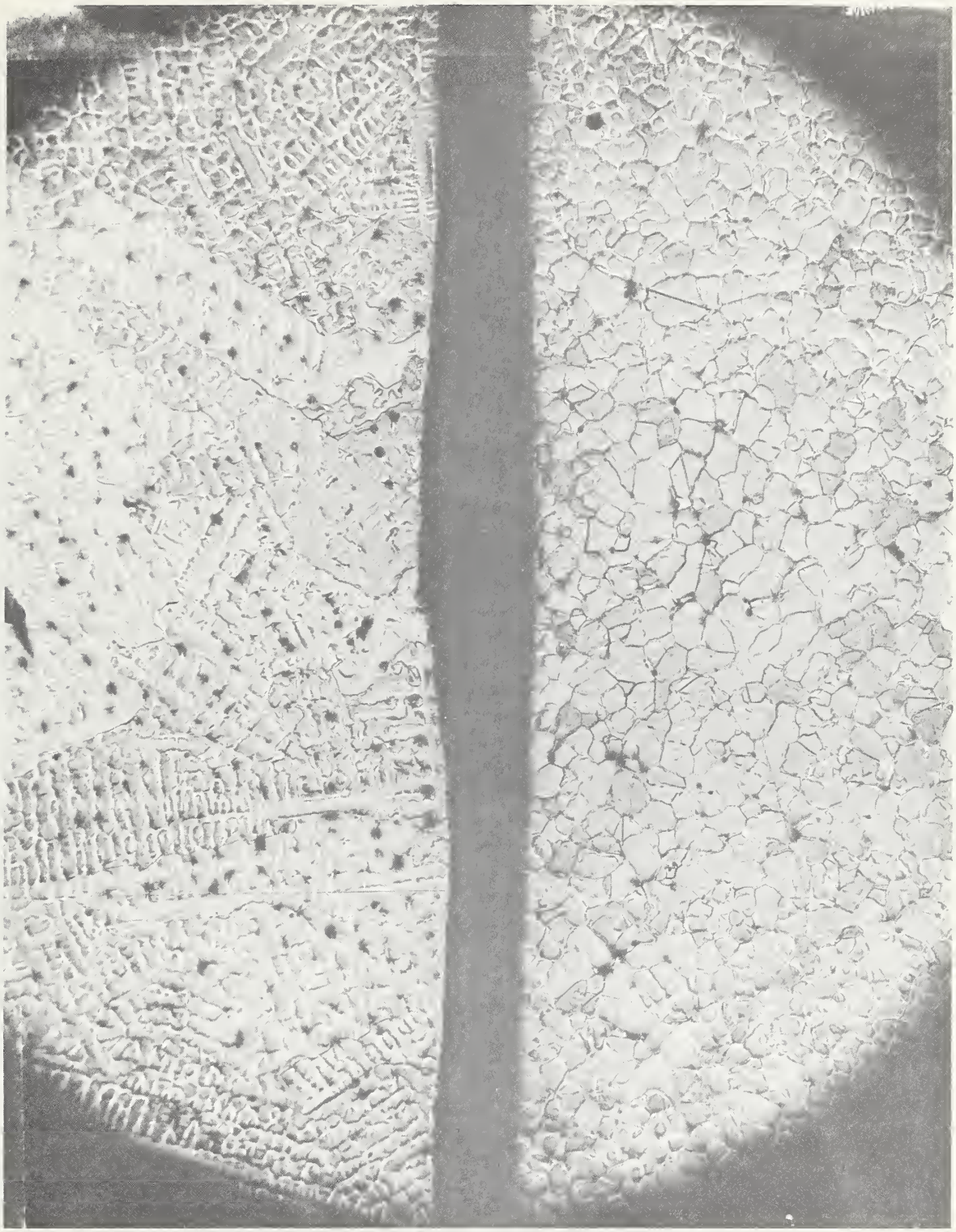

Figure 3. Coarse grained and fine grained alloy, Type III

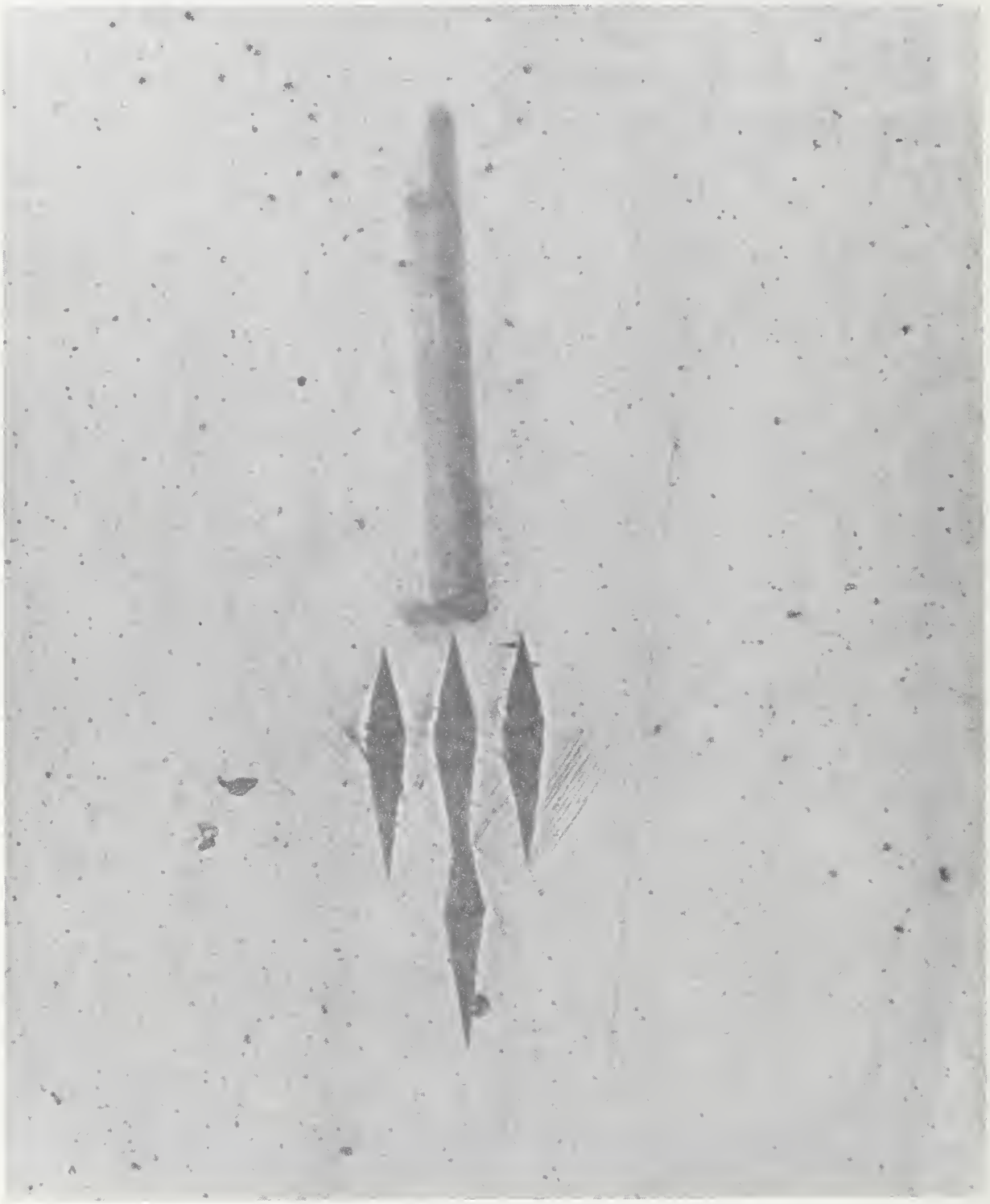

Figure 4. Coarse grained, base, Type III

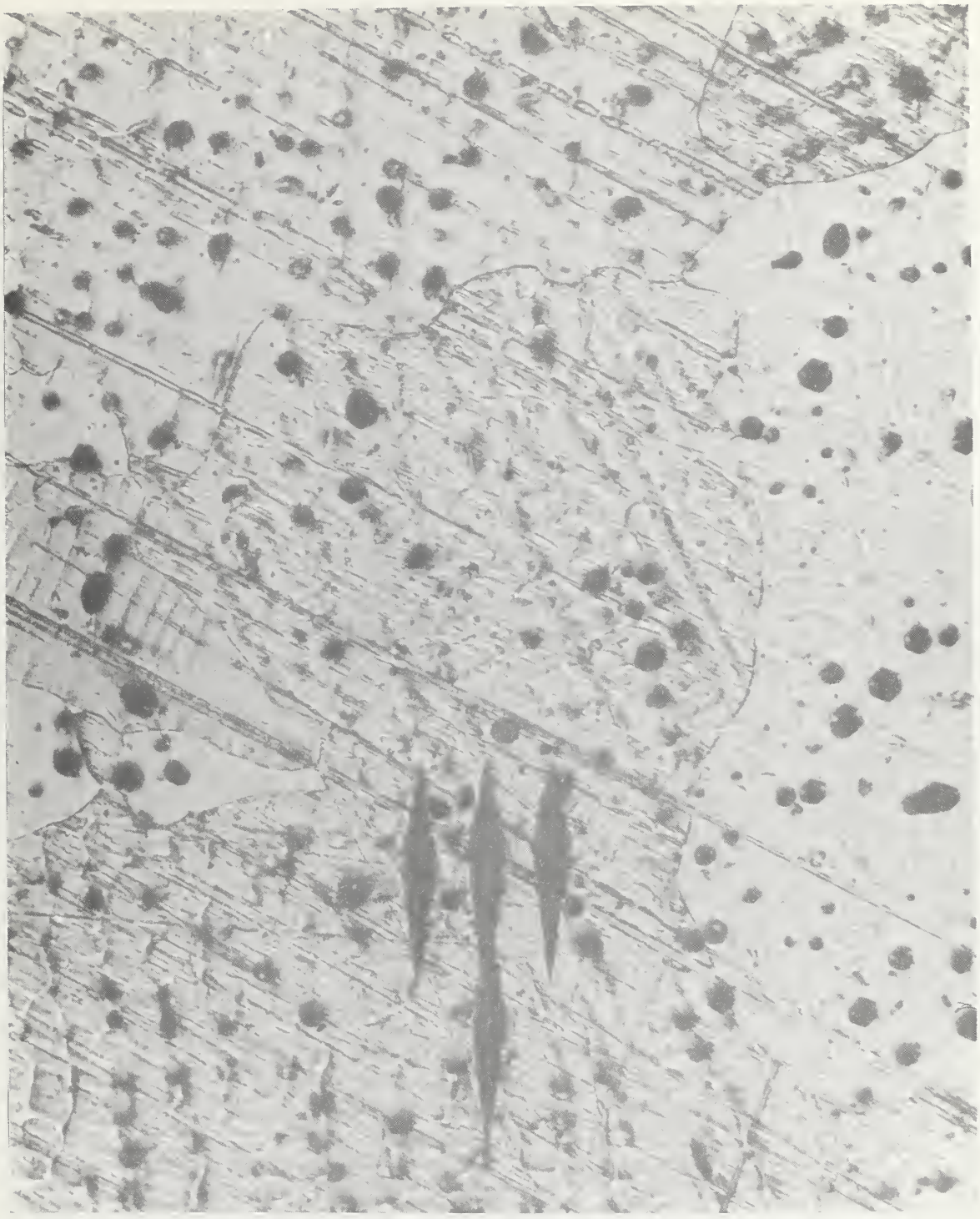

Figure 5. Coarse grained, base. Type III

TYPE III
COARSE GRAINED, BASE

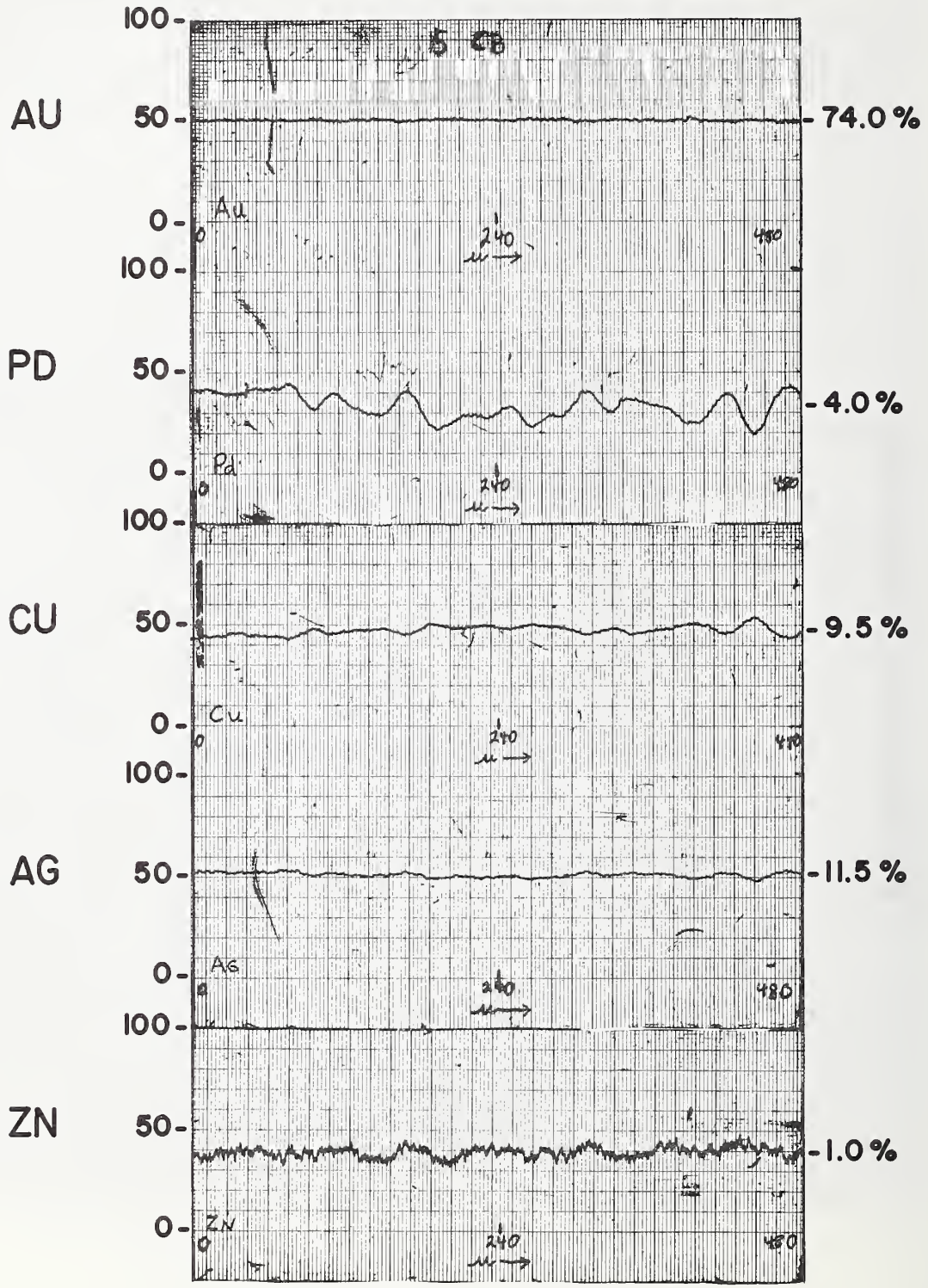

Figure 6. Coarse grained, base, Type III.

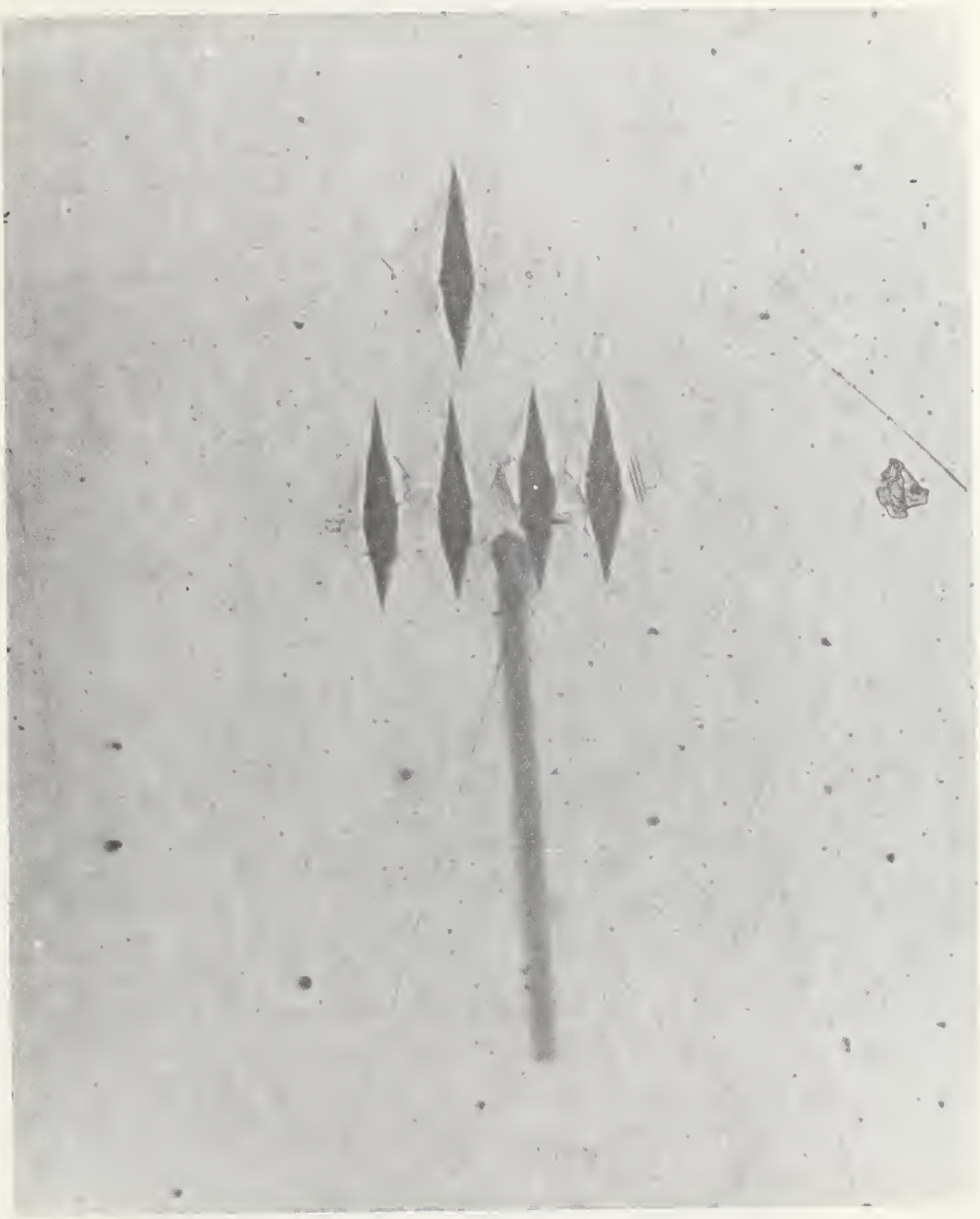

Figure 7. Fine grained, tip, Type III

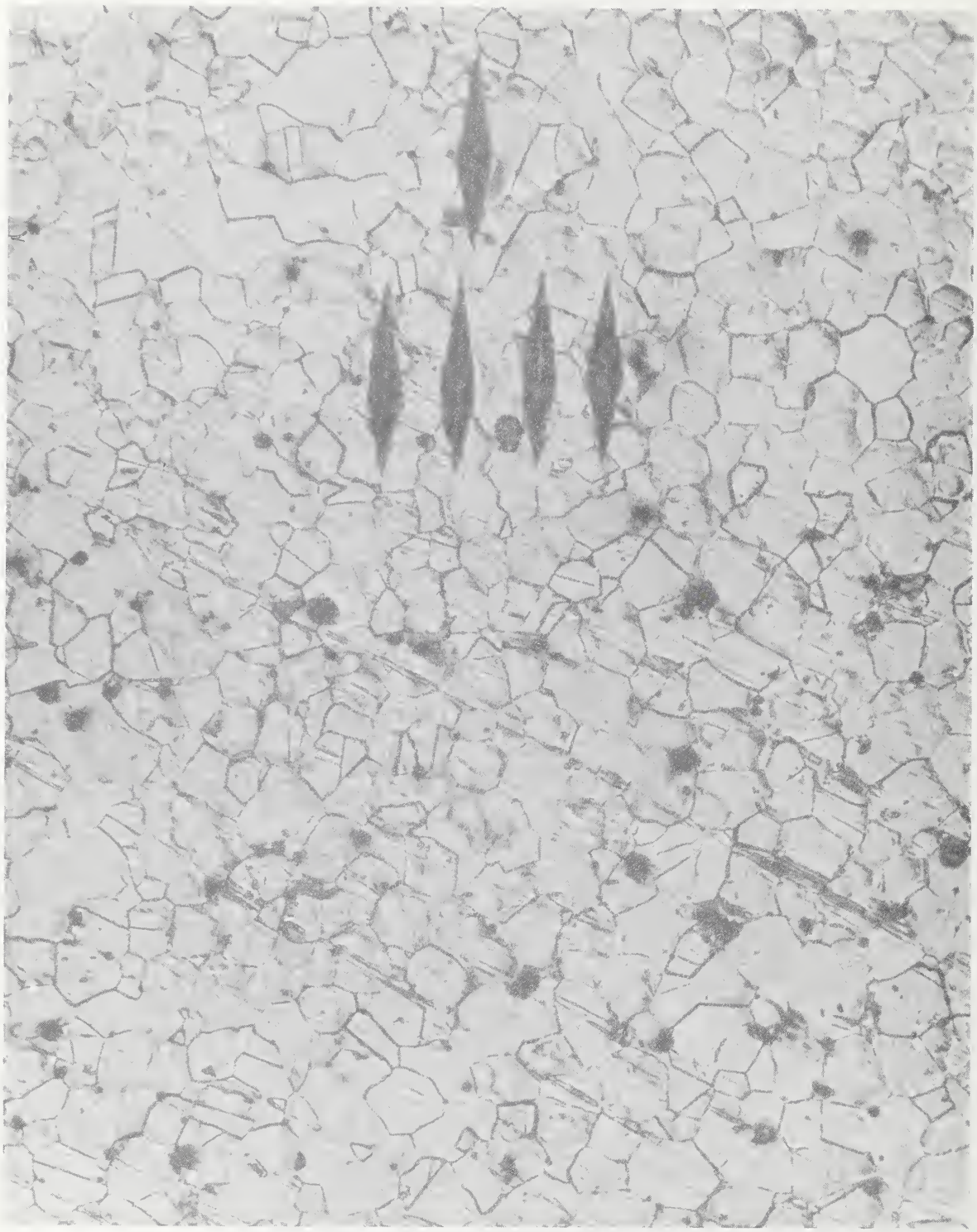

Figure 8. Fine grained, tip, Type III

TYPE III
FINE GRAINED, TIP

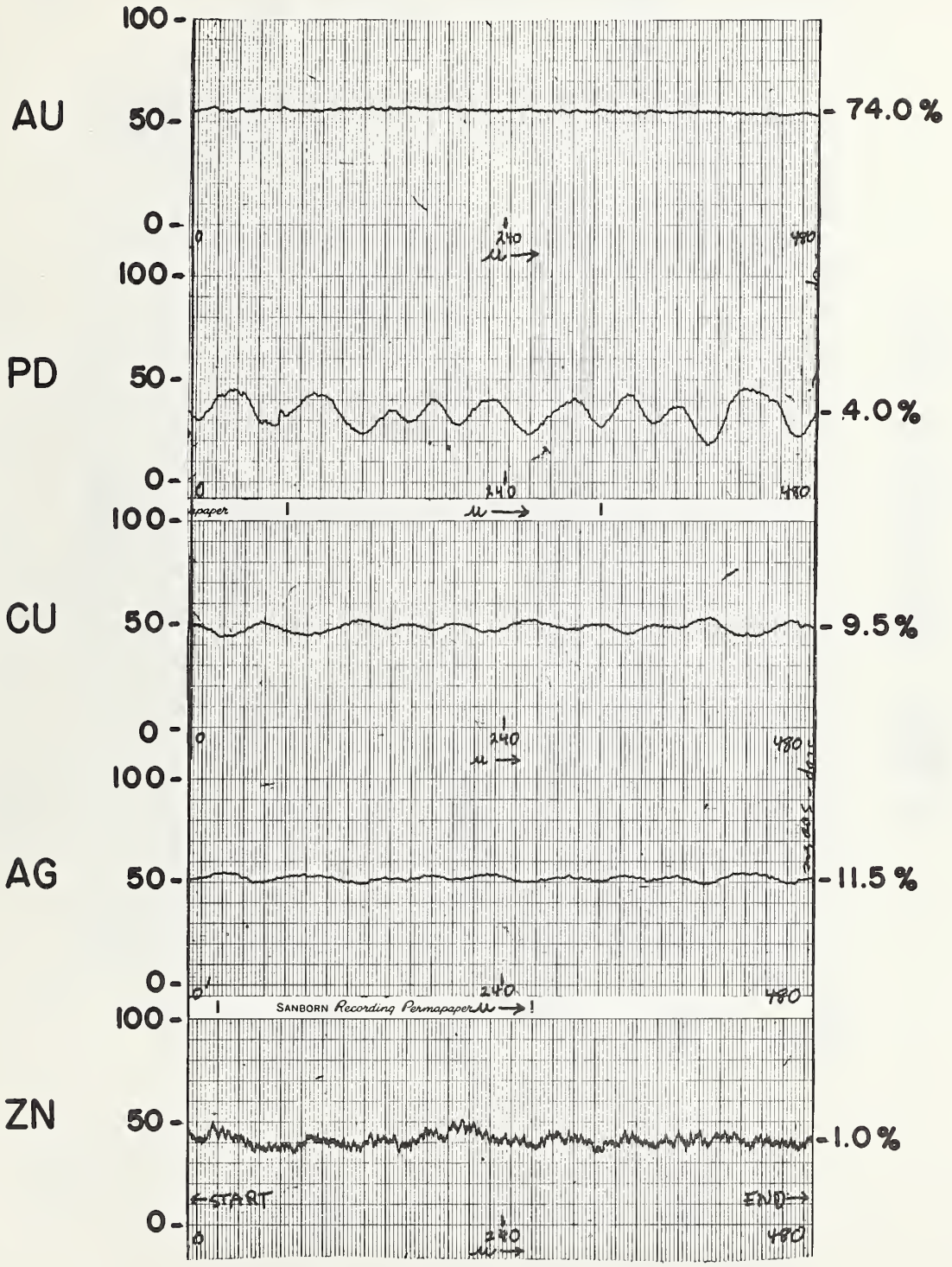

Figure 9. Fine grained, tip, Type III.

TYPE III
FINE GRAINED, TIP

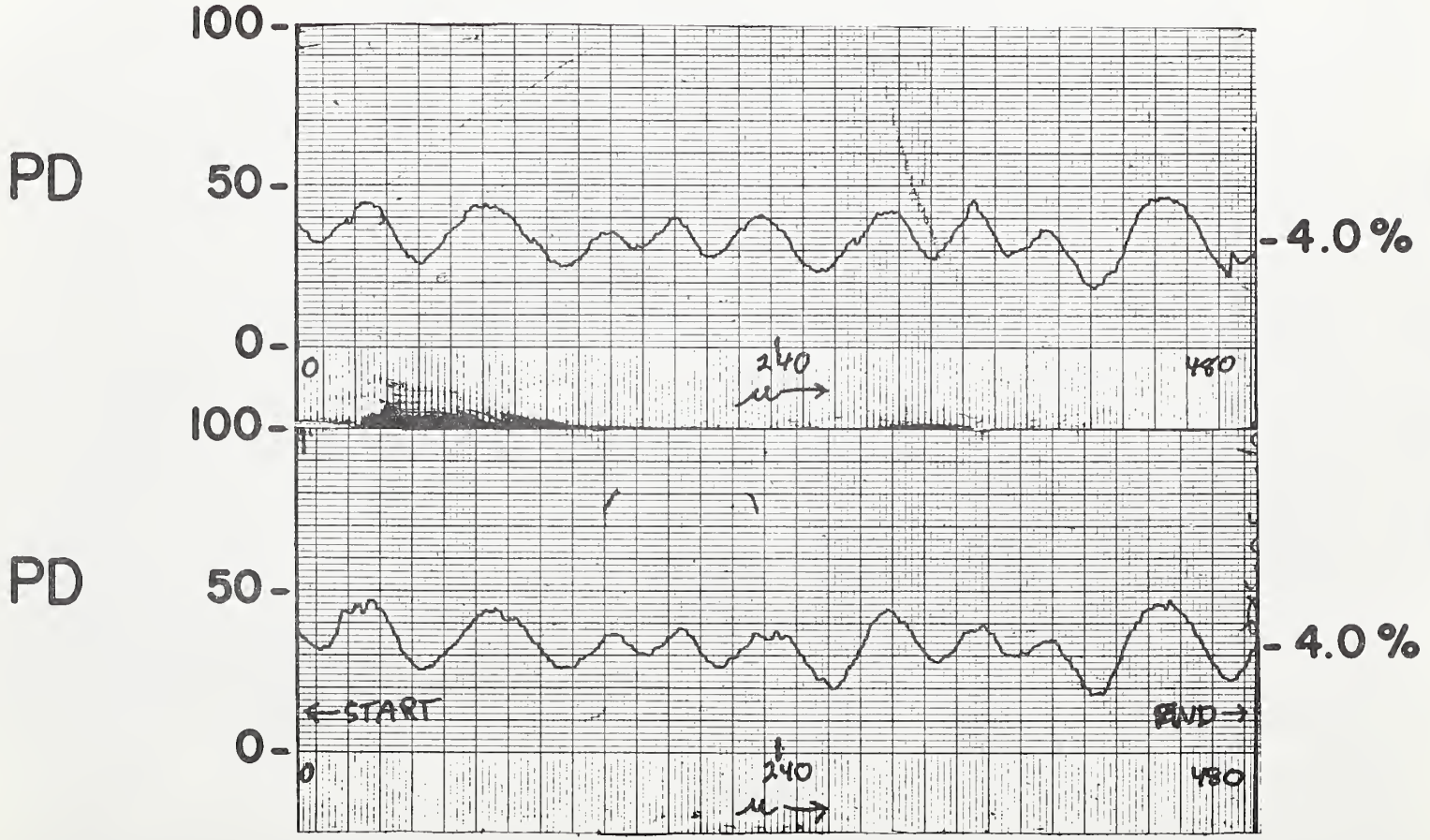

Figure 10. Fine grained, tip, Type III.

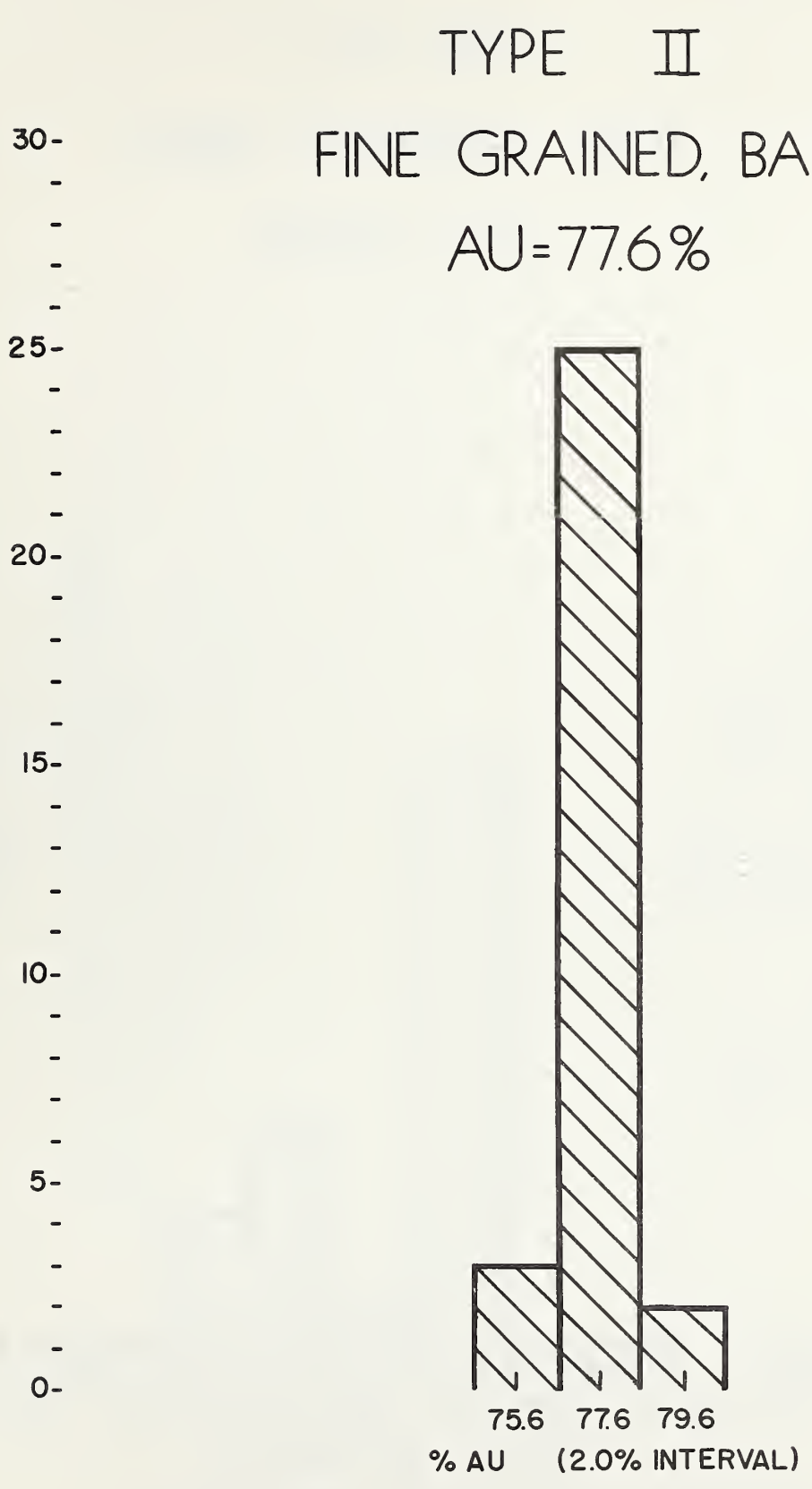

Figure 11. Fine grained base, Type II.

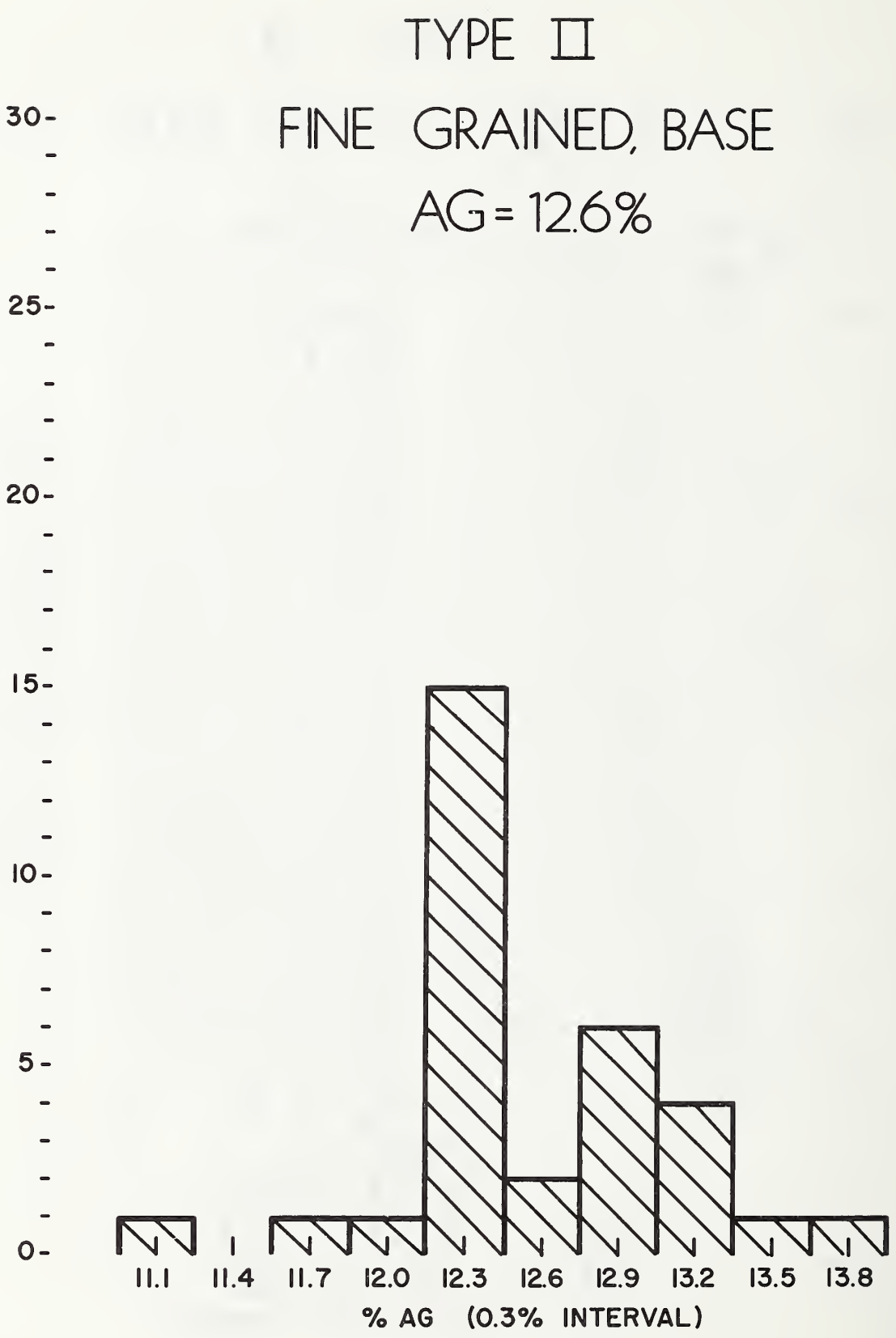

Figure 12. Fine grained, base, Type II

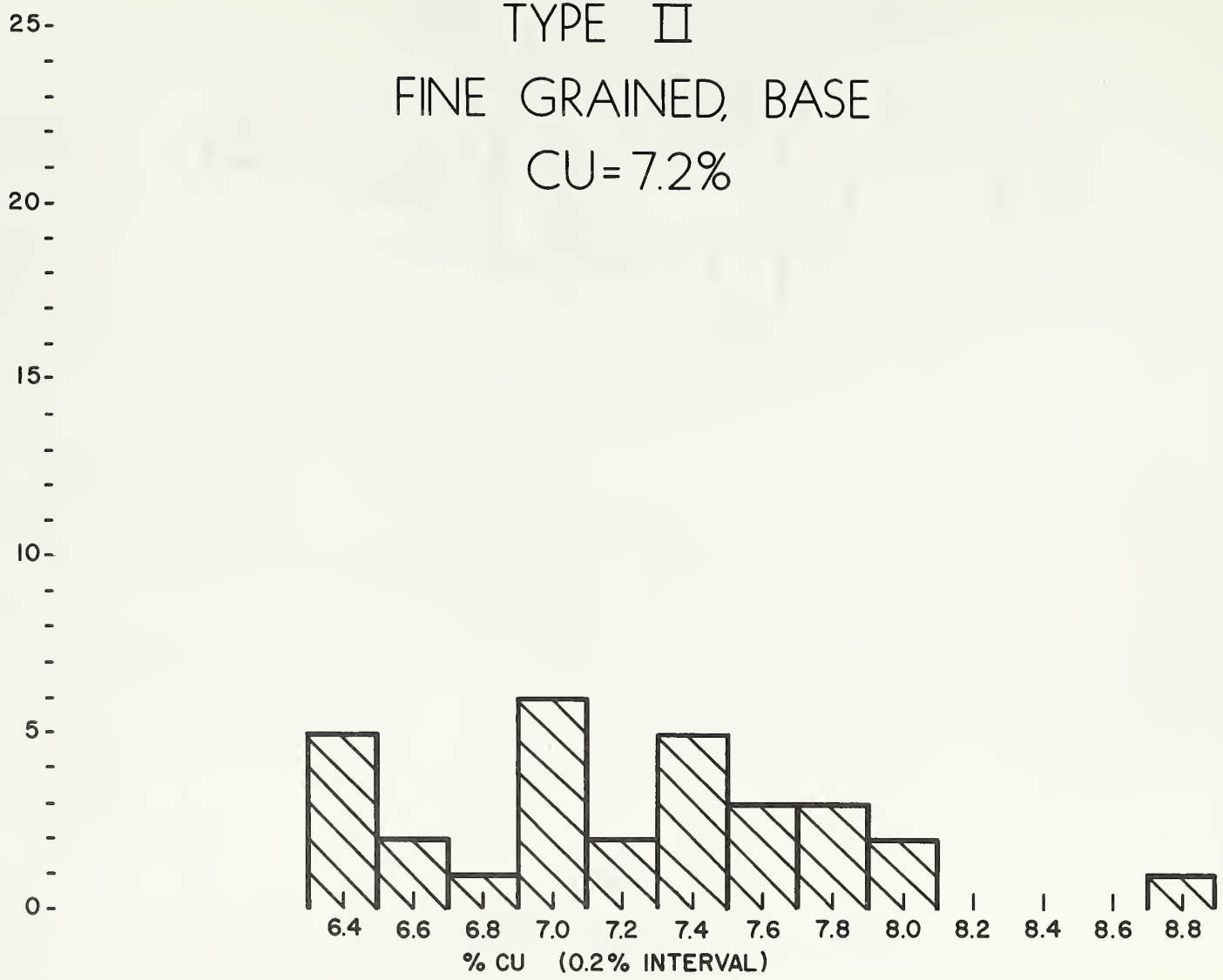

Figure 13. Fine grained, base, Type II.

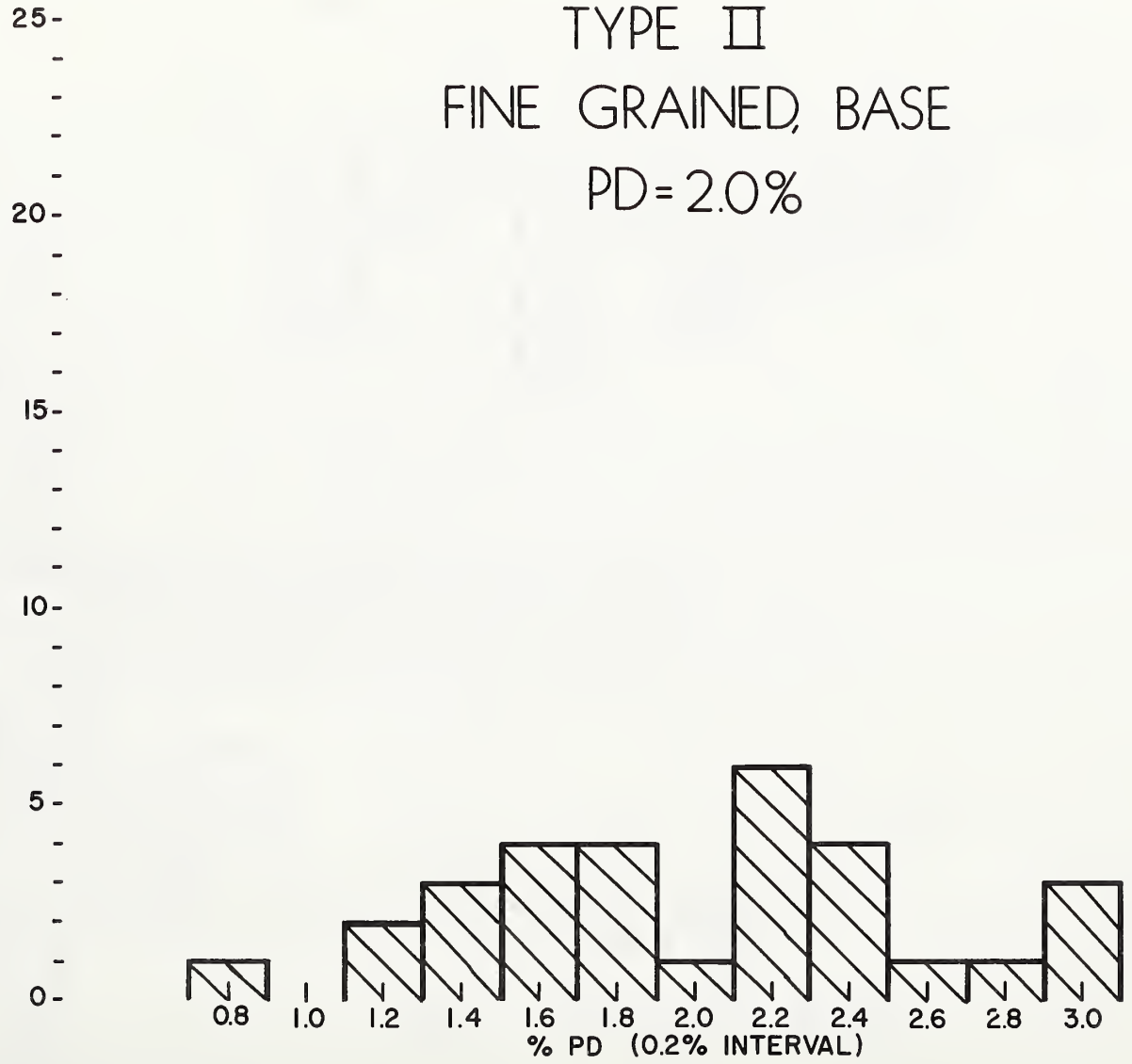

Figure 14. Fine grained, base, Type II.

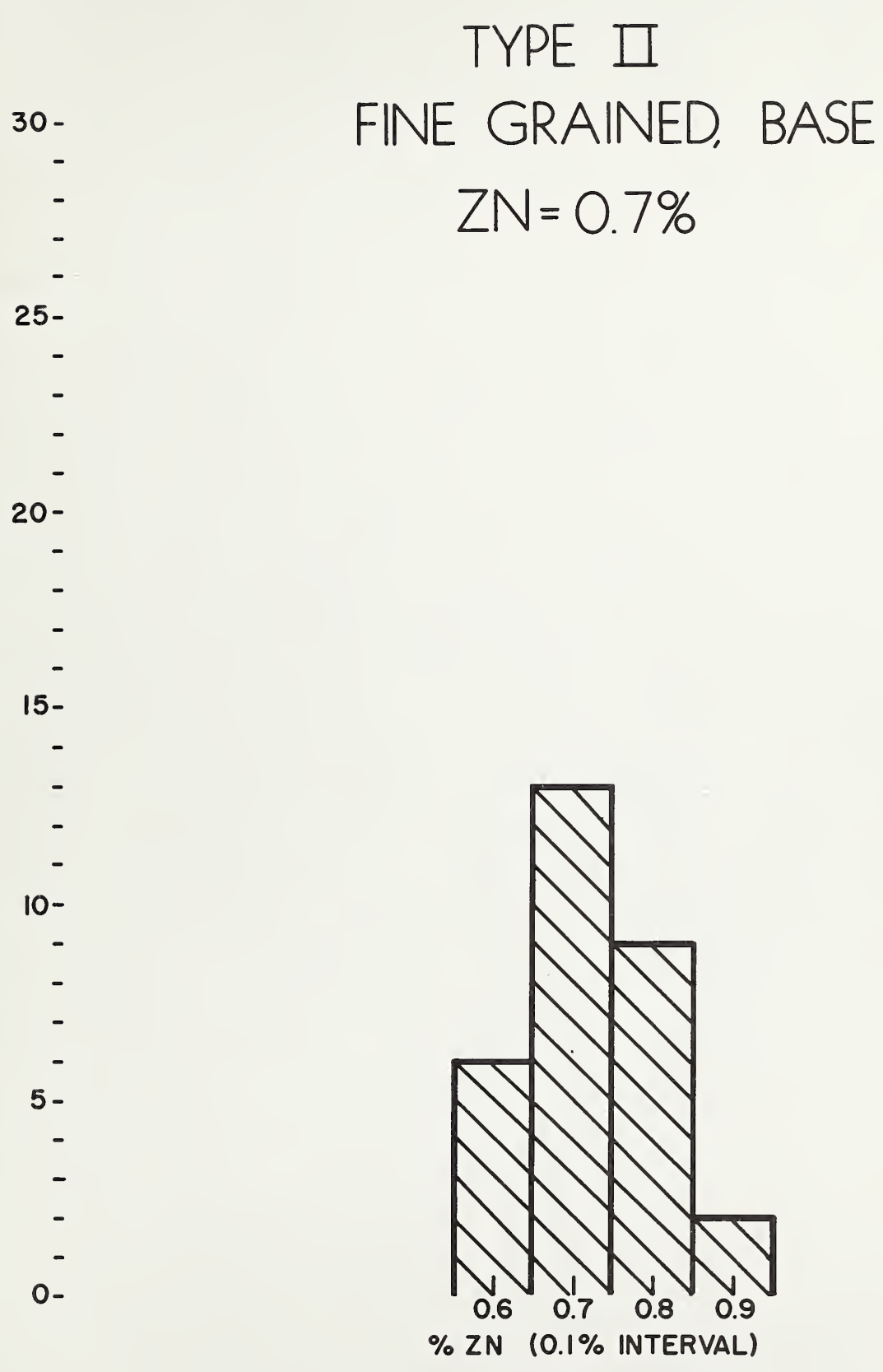

Figure 15. Fine grained, base, Type II.

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